

After-Cooking Discoloration of Potatoes Role of the Organic Acids

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SUMMARY

Stem- and bud-end tissue from 41 samples of potatoes representing various degrees of after-cooking discoloration were analyzed for organic acids content. The individual acids determined were glutamic, aspartic, pyroglutamic, malic, citric, orthophosphoric, oxalic, and one unidentified acid. The stem-end tissue contained a lower concentration of all the acids except the unidentified one. The difference between the stem- and bud-end was very large in some cases, notably for malic acid and citric acid.

Examination of the data indicated a strong tendency for degree of blackening to be associated with low organic acid content. A statistical analysis of the data showed highly significant correlation of low citric acid, orthophosphoric acid, and oxalic acid content with blackening. Citric acid exhibited the highest degree of correlation, having an r value of 0.768.

The significant correlation between low citric acid content and after-cooking blackening was maintained in all but one case when subgroups of the samples were formed according to variety, crop year, and location grown. Of the three varieties studied statistically, Ontario and Katahdin showed correlation, whereas Kennebec did not.

The interrelationships of iron, citric acid, and potassium contents were studied. Since there is always a large excess of citric acid over iron, it must be assumed that something prevents the citric acid from chelating the iron in blackening potatoes. The data indicate that potassium may be the main constituent playing this role. In the final analysis, the primary factor in the blackening phenomenon is probably the amount of free organic acid present.

INTRODUCTION AND LITERATURE REVIEW

Several previous publications (Yanovsky, 1955; Hunter *et al.*, 1957; Heisler *et al.*, 1962, 1963) from this laboratory have described the problem of after-cooking discoloration of potatoes. Briefly stated, this is a discoloration that occurs only after cooking and is not observed in the raw tissue. It appears at the surface shortly after cooking, during cooling, and is generally more intense at the stem end than at the bud end of the tuber. It is now generally accepted that the discoloration is due to the formation of a dark-colored complex of iron and chlorogenic acid, but it is also recognized that the presence or absence of other constituents plays a major role in the blackening mechanism.

The role of citric acid, because of its known ability to chelate iron, has been given prime consideration. From the practical standpoint, most of the proposed methods of treating potatoes to alleviate the after-cooking discoloration are based on the chelating principle (Greig and Smith, 1955; Hawkins *et al.*, 1959; Hunsader and Henning, 1958; Smith and Davis, 1962).

Juul (1949) showed that the discoloration was influenced by citric acid. However, he attributed this influence to a pH effect. Mulder (1949) and Bate-Smith *et al.* (1958) recognized the citric acid action as a chelating effect and stated that the distribution of blackening in individual cooked tubers is governed mainly by the competition between chlorogenic acid and citric acid for iron. Hughes and Swain (1962b) studied

the effect of citric, orthophosphoric, and malic acid on the color of various phenol-iron complexes (*in vitro*) and concluded that citric acid was the most important of these factors in reducing the intensity of color of the chlorogenic acid-iron complex.

In spite of the apparent importance of citric acid and perhaps other organic acids, the literature reports no general and intensive study of the organic acid content of potatoes and their relationship to stem end blackening. Hughes and Swain (1962a) studied the citric and phosphoric acid content of four individual tubers and reported correlation of blackening with the ratio of citric acid to chlorogenic acid. While this was sufficient for their purpose of establishing the importance of citric acid in relation to blackening, we felt that a more general analytical study of a large number of samples would be of value.

Thus, in an attempt to gain more information on the organic acids content of potatoes and their possible effect on after-cooking discoloration, we have determined the organic acids content of the stem and bud ends of a large number of samples representing a wide range of discoloration and have made a statistical study of the data.

EXPERIMENTAL METHODS

Potatoes. The 41 samples of potatoes used in these experiments were sent to us as blackening samples from various parts of the country over a three-year period. Most were received from Wisconsin (19 samples) and Michigan (15), with the remainder coming from Pennsylvania (3), Maine (3), and Long Island (1).

The experimental details for obtaining the sample and determining the degree of discoloration have been presented (Heisler *et al.*, 1962). For convenience, a brief outline is given here.

Potato sampling. Plugs were taken from the stem- and bud-end sections of thoroughly washed and scrubbed potatoes using a no. 15 cork borer. The plugs were cut to a length of approximately 1 in. and then cut in half lengthwise. One half was used for the organic acids determination and the other for measurement of degree of discoloration by a reflectance test. The half cylinders used for the organic acids determination were adjusted in length so that 26 pieces totaled 100.00 g. Those used for the reflectance measurement were adjusted to total weight of 65.00 g.

Determination of degree of discoloration. The

reflectance obtained from a smooth surface (under glass) of cooked mashed potato was taken as a measure of discoloration. The reflectance attachment to the Beckman Model B spectrophotometer (no endorsement implied) was used, with MgCO_3 as standard. In this study, "degree of discoloration" was arbitrarily taken as $(R_B - R_S)/R_S$, where R_B is the reflectance of mash from the bud end, and R_S represents that for the stem end. The more discoloration in the potato, the greater the difference between R_B and R_S and the lower the value of R_S . Thus, these factors reinforce each other to amplify the value for degree of discoloration, making the system more sensitive in differentiating samples.

Preparation of extract. The 100.00-g sample of potato tissue (26 half-plugs from stem or bud end) was ground for 2 min in 300 ml of iron-free water (redistilled in all glass apparatus and checked with reagent) in a Waring blender. The slurry was filtered through Whatman no. 12 paper. The filtrate was immersed in a boiling water bath for 5 min to coagulate the protein and then filtered, while hot, through Whatman no. 12 paper. Loss of vapor during heating and filtering was kept to a minimum by stoppering the flask with a ground-glass stopper and by covering the funnel with a watch glass. The filtrate obtained in this way contained about 1% solids. The individual organic acids of the deproteinized extract were determined.

The resulting samples of deproteinized extracts, though prepared by the same procedure, varied slightly in solids content because of differences inherent in the various lots of potatoes. The exact solids content of each extract was determined by loss of weight after drying. The individual organic acids were determined as the quantity present in the deproteinized extract, but it can be related, percentage-wise, to the fresh potato weight or to the solids content of the juice.

While it is recognized that the above procedure is not an exhaustive extraction it was believed sufficient for the purpose of determining differences in the organic acids content of various samples and between the stem and bud end of the same sample.

Determination of the individual organic acids. The method of Schwartz *et al.* (1962) was used. This method utilizes an anion-exchange resin to adsorb the acids, and a gradient-elution technique to elute and fractionate the acids from the column. The individual fractions were then titrated with base.

RESULTS AND DISCUSSION

Forty-one samples, representing a wide range of after-cooking discoloration, were

analyzed for organic acids content. The stem- and bud-end samples of deproteinized extracts were studied. Table 1 lists the 41 samples in order of decreasing degree of discoloration, giving the organic acids content of the stem- and bud-end tissue. Table 2 shows the range of values and the average value for the stem and bud ends and for the difference between the bud and the stem ends. The orthophosphoric and oxalic acids were treated as one because separation of these two acids was not complete in every case. In general, the stem end contained a lower concentration of all the acids except the unknown. The difference between the stem and bud end in some cases is very large, notably for malic and citric acids. The stem-end values have a wider range for all the acids except glutamic and the unknown, the most variation occurring with malic acid.

Examination of all data for the 41 samples shows a strong tendency for degree of blackening to be associated with low organic acid content of the stem end, especially in the case of citric and malic acids. Considering the fact that the stem end blackens and the bud end does not, the bud end of each sample can be considered a control and the organic acid value for the difference between the stem and bud ends should be related to the tendency to blacken. As expected, this value does show a direct relationship to blackening, that is, the bud-stem difference value increases with tendency to blacken. Thus, low organic acid content in the stem end and a large difference in the organic acid content of the stem and bud ends tends to be associated with blackening. By combining these two factors in the ratio $(OA_B - OA_S)/OA_S$ (where OA_B is the organic acid content of the bud end, and OA_S that of the stem end), similarly to that done for reflectance values, one arrives at an expression for organic acid content that should give the highest degree of correlation with blackening. Figs. 1 and 2 are plots of these four functions (stem, bud, bud minus stem, bud minus stem/stem) for the citric acid data and the total organic acid data against degree of blackening. It can be observed that the value of (bud minus stem)/stem

gives a much better distribution of points than the other values, especially in the case of the total organic acid content.

A statistical study was made of all the organic acid data by the linear regression method, and an analysis of variance was made. Table 3 gives the F and the r values obtained, indicating the extent of correlation. As stated before, since only the stem end blackens, correlation between the degree of discoloration and organic acid content should be obtained for the values of stem, bud minus stem, and (bud minus stem)/stem, but not for the bud value. This theoretically ideal situation is obtained only with the values for citric acid and for orthophosphoric + oxalic acid. The malic acid results display an anomaly in that the bud-end value shows significance whereas the bud-minus-stem difference value does not. Citric acid shows the highest degree of correlation. The highest r value obtained was 0.768, for the (bud minus stem)/stem (citric acid data). This would give an r^2 of 0.591, indicating that 59% of the variability of blackening is due to this ratio. This is still too low for prediction purposes, so no attempt was made to determine confidence levels.

The significant correlation between low citric acid content and degree of discoloration was maintained in all but one case when subgroups of the samples were formed according to location grown, crop year, and variety. Table 4 summarizes the results of this statistical analysis of the subgroups. Of the three varieties studied, two (Ontario and the Katahdin) showed significant correlation of low citric acid content and blackening. The high r values obtained for the (bud minus stem)/stem function of these two varieties indicate that this value could perhaps be used to predict whether a particular sample will discolor. The Kennebec variety failed to exhibit correlation. When the potato samples from Wisconsin and Michigan were treated separately, both groups showed highly significant correlation of citric acid content and blackening. Also, considering the samples on a yearly basis, a significant correlation was obtained for the three years over which the study extended.

Table 1. Organic acid values and their relation to after-cooking discoloration.

Sample	Variety	$\frac{R_p-R_s}{R_s}$	Mg per 100 ml										Meq per 100 ml					
			Glutamic		Aspartic		Pyroglutamic		Malic		Citric		O-Phosphoric + Oxalic		Unknown		Totals	
			Stem	Bud	Stem	Bud	Stem	Bud	Stem	Bud	Stem	Bud	Stem	Bud	Stem	Bud	Stem	Bud
59-23	Wisc. Antigo	0.697	14.7	12.9	15.7	20.5	5.3	15.4	2.2	19.4	23.0	167.6	.410	.692	.528	.338	1.58	4.25
59-24	Wisc. Red Lasoda	0.695	15.9	15.9	18.5	16.3	6.6	6.7	2.4	11.7	26.1	140.7	.468	.760	.403	.345	.160	3.72
59-19	Wisc. Katahdin	0.623	15.6	16.6	18.7	17.6	6.6	9.7	2.5	16.7	33.8	147.9	.389	.760	.619	.528	1.86	4.13
59-20	Wisc. Kennebec	0.572	16.3	16.5	20.8	24.7	5.4	11.3	2.2	15.8	29.6	154.8	.410	.736	.407	.266	1.61	3.99
59-25	Wisc. Red Lasoda	0.522	16.9	16.4	18.5	18.9	5.7	6.8	2.6	14.9	41.0	184.3	.536	.793	.486	.432	1.99	4.57
59-15	Wisc. Early Gem	0.519	14.4	15.1	18.4	24.3	7.1	14.1	3.5	24.0	32.5	144.0	.303	1.029	.396	.310	1.54	4.01
61-1	Mich. Ontario	0.516	8.3	10.8	17.5	15.9	5.5	9.7	2.0	20.5	14.0	91.2	.413	.509	.522	.347	1.41	2.82
61-3	Mich. Huron	0.503	5.5	7.2	12.9	16.2	4.4	6.8	2.5	26.3	21.1	141.6	.383	.654	.421	.329	1.33	3.90
59-22	Wisc. Antigo	0.497	14.5	14.4	18.2	19.7	6.0	10.1	3.2	22.3	34.6	160.6	.365	.677	.515	.304	1.89	4.10
59-18	Wisc. Katahdin	0.475	15.1	15.3	19.0	17.1	8.4	7.7	2.7	16.2	33.5	140.8	.326	.620	.656	.462	1.85	3.77
60-1	Pa. Merrimack	0.469	8.0	10.5	22.2	21.4	6.7	8.8	3.4	23.2	26.5	128.7	.477	.757	.684	.448	1.72	3.82
60-2	Pa. Merrimack	0.449	7.8	19.7	19.5	22.2	10.4	13.7	3.3	39.3	20.8	131.2	.440	.675	.663	.438	1.76	4.11
61-2	Mich. Ontario	0.434	9.1	10.1	18.8	18.0	5.4	9.7	2.4	19.0	26.3	112.6	.365	.689	.484	.341	.153	3.32
60-3	Pa. Merrimack	0.421	9.5	12.0	17.1	15.0	7.8	9.3	5.2	20.8	33.2	149.0	.501	.771	.663	.382	2.00	4.01
60-5	Wisc. Antigo	0.405	13.9	13.6	18.4	18.2	5.6	5.3	8.0	29.3	43.4	119.8	.429	.586	.429	.299	1.92	3.42
61-5	Wisc. Kennebec	0.396	7.9	5.9	19.7	20.1	12.3	12.1	16.7	33.9	87.1	173.6	.593	.740	.646	.414	3.12	4.60
60-4	Me. Katahdin	0.332	9.5	10.5	22.9	20.6	7.1	8.1	4.4	24.2	69.0	185.8	.468	.718	.610	.390	2.49	4.59
60-7	Wisc. Katahdin	0.332	10.2	14.1	18.1	15.0	6.2	6.6	7.7	30.5	62.1	144.0	.486	.716	.540	.420	2.35	4.04
59-16	Wisc. Early Gem	0.322	11.1	12.6	19.3	24.6	4.3	12.2	2.5	24.8	82.4	182.5	.316	.832	.405	.300	2.27	4.66

59-13 Mich. Huron	0.306	11.8	11.4	18.5	18.0	8.7	13.2	18.0	29.8	94.8	176.0	.656	.826	.383	.282	3.01	4.42
61- 6 Wisc. Katahdin	0.269	7.2	10.0	21.0	19.3	9.5	9.1	19.2	40.6	94.7	179.8	.663	.776	.586	.372	3.26	4.78
59-17 Wisc. Ontario	0.259	11.3	8.5	17.1	21.3	6.6	11.1	8.7	26.4	58.8	153.4	.394	.736	.622	.466	2.28	4.22
61- 7 Me. Kennebec	0.256	6.4	7.1	24.3	21.1	8.9	8.2	14.9	36.0	76.7	141.0	.602	.657	.541	.382	2.83	3.99
60- 6 Wisc. Red Lasoda	0.239	10.9	14.3	20.7	21.6	7.2	7.9	7.8	21.6	90.4	183.3	.577	.767	.690	.459	3.05	4.67
60-16 Mich. Huron	0.235	4.7	4.9	17.9	20.0	5.7	7.4	10.0	35.0	60.1	174.8	.481	.664	.561	.342	2.32	4.43
60-11 Mich. Ontario	0.204	6.6	6.2	19.1	19.6	5.3	6.7	4.3	30.5	26.9	93.6	.366	.561	.481	.378	1.55	3.05
60-12 Mich. Ontario	0.183	7.5	7.9	19.4	18.3	5.6	7.4	16.4	30.9	65.4	112.6	.565	.620	.427	.351	2.47	3.39
61- 4 L. I. Katahdin	0.162	11.0	12.7	17.7	18.1	12.3	9.3	6.2	24.6	96.6	203.0	.532	.947	.622	.310	3.03	4.90
59-14 Mich. Cherokee	0.150	17.2	13.6	21.4	17.8	10.4	8.9	8.3	20.8	82.2	154.8	.629	.697	.381	.196	2.75	3.87
60- 9 Wisc. Kennebec	0.134	11.1	11.4	19.6	19.4	8.3	9.3	21.8	38.8	92.6	170.4	.557	.798	.665	.446	3.23	4.72
60-10 Wisc. Ontario	0.128	11.1	10.3	20.0	18.2	8.8	10.0	20.6	35.5	76.9	126.4	.541	.752	.676	.500	3.03	3.99
60-13 Mich. Ontario	0.124	6.2	7.3	21.8	21.2	5.2	7.1	7.7	28.3	60.0	133.8	.477	.629	.465	.353	2.22	3.70
60-19 Mich. Ontario	0.095	12.7	12.0	23.6	20.8	7.3	8.8	10.7	30.2	60.5	145.4	.462	.663	.574	.383	2.26	4.02
59-12 Mich. Manota	0.069	0.7	5.1	22.9	24.7	10.4	12.0	15.3	22.2	103.6	158.0	.598	.798	.362	.300	3.13	5.00
60- 8 Wisc. Early Gem	0.052	12.1	11.7	22.1	17.2	13.5	12.5	21.4	31.8	63.5	149.8	.433	.812	.640	.444	2.77	4.33
61- 8 Me. Katahdin	0.052	8.1	10.3	20.5	21.3	4.9	8.2	14.7	37.6	72.0	143.4	.568	.740	.624	.494	2.75	4.27
60-14 Mich.?	0.015	5.1	4.9	21.5	23.7	4.1	6.7	11.4	36.4	75.7	159.6	.549	.746	.554	.407	2.65	4.39
60-17 Mich. Cherokee	0.010	12.0	11.9	18.3	20.4	4.8	7.3	5.3	17.9	55.6	178.4	.445	.648	.423	.325	2.65	4.26
60-18 Mich. Russet Rural	0	9.9	12.5	19.3	20.6	6.7	5.5	16.9	31.4	48.8	151.4	.495	.645	.425	.438	2.17	4.09
59-21 Wisc. Kennebec	0	13.3	13.7	20.0	23.0	7.6	14.7	8.8	26.9	77.9	216.0	.596	.862	.431	.340	2.65	5.29
60-15 Mich. Russet Rural	0	9.8	10.8	15.3	16.9	7.2	7.4	22.7	41.7	93.3	154.5	.409	.604	.352	.330	2.76	4.17

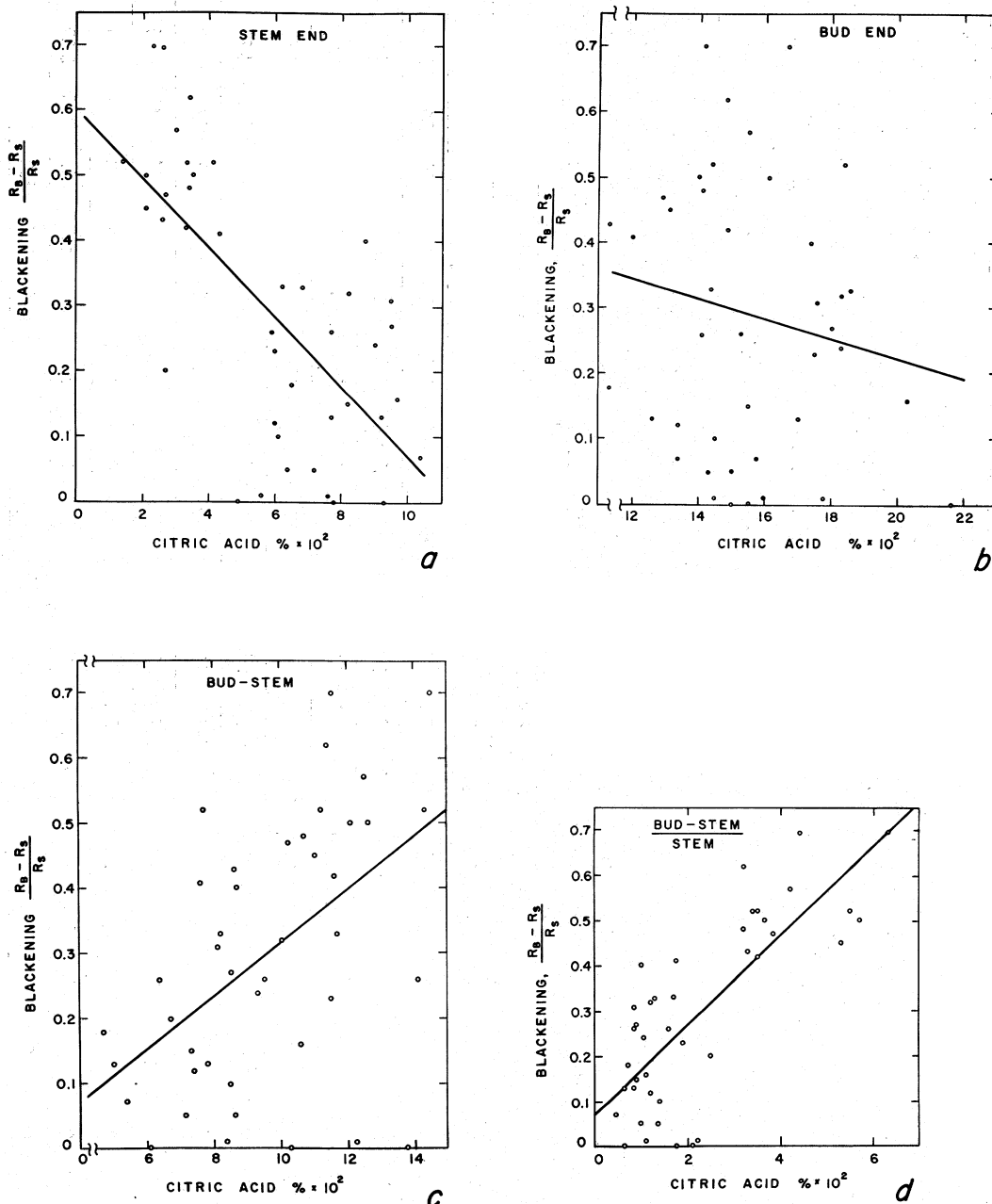


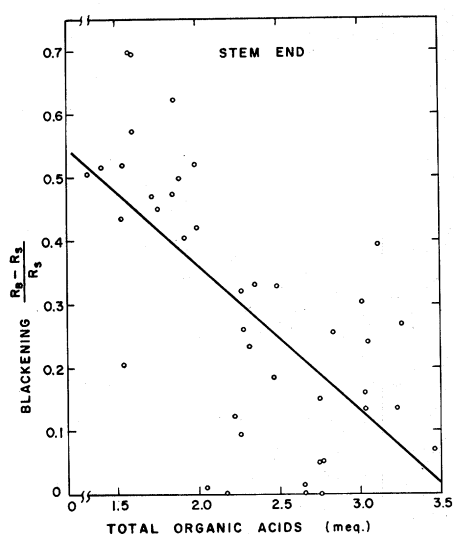
Fig. 1. Variation of degree of discoloration with the citric acid content. (a) Stem end, (b) bud end, (c) bud minus stem, (d) ratio of bud minus stem to stem.

The interrelationships of some of the constituents studied in this and previous publications from this laboratory (Heisler *et al.*, 1962, 1963) were investigated. It was found that the ratio of iron/citric acid on

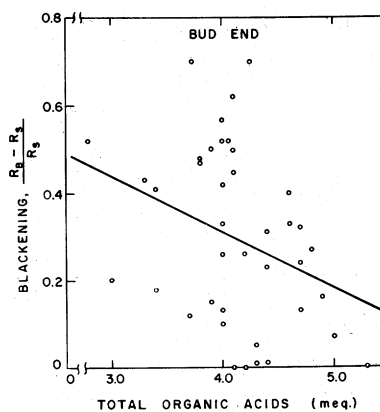
a molar basis gave a slightly higher degree of correlation with blackening than either iron or citric acid alone (see Fig. 3 and Table 5). The r value for the stem-end data was increased from 0.680 to 0.777 ($r^2 =$

Table 2. Range of organic acid values for 41 samples.

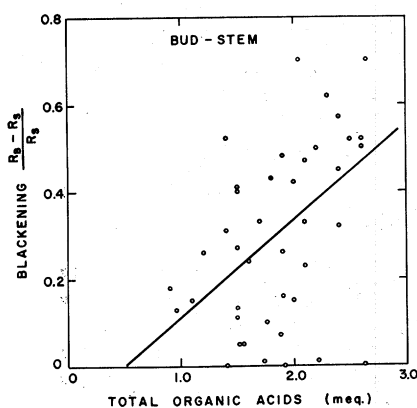
	Stem			Bud			Bud-stem Av.
	High	Low	Av.	High	Low	Av.	
Mg/100 ml							
Glutamic	17.2	04.7	10.7	19.7	04.9	11.4	0.7
Aspartic	24.3	12.9	19.4	24.7	15.0	19.7	0.3
Pyroglutamic	13.5	04.1	07.2	15.4	05.3	09.4	2.2
Malic	22.7	02.0	09.0	41.7	11.7	27.0	18.0
Citric	93.3	14.0	57.7	216.0	91.2	152.8	95.1
Meq/100 ml							
o-Phosphoric							
+ oxalic	0.66	0.30	0.48	1.03	0.51	0.72	.24
Unknown	0.69	0.32	0.53	0.53	0.20	0.38	-.15
Total	3.26	1.33	2.29	5.29	2.82	4.14	1.85



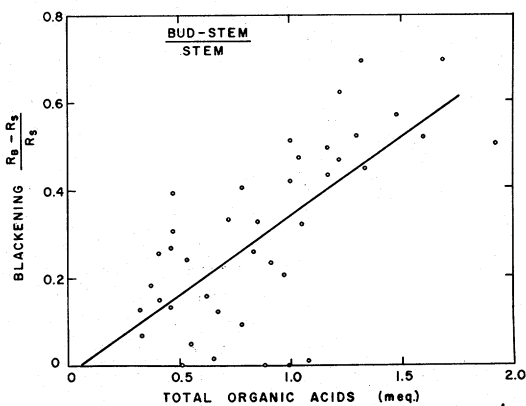
a



b



c



d

Fig. 2. Variation of degree of discoloration with the total organic acids content. (a) Stem end, (b) bud end, (c) bud minus stem, (d) ratio of bud minus stem to stem.

Table 3. Summary of statistical study of organic acid data.

Acid	Stem		Bud		Bud-stem		Bud-stem/ stem	
	F	r	F	r	F	r	F	r
Glutamic	5.55*	.352*	9.34**	.438**	< 1	.095
Aspartic	5.65*	.356*	1.58	.198	< 1	.114
Pyroglutamic	$\cong 1$.192	$\cong 1$.184331**
Malic	31.38**	.667**	18.46**	.568**	< 1	19.86**	.580**
Citric	33.58**	.680**	$\cong 1$.203	12.90**	.498**	56.59**	.768**
o-Phosphoric + oxalic	8.77**	.427**	$\cong 1$	4.73*	.329*	4.18*	.312*
Unknown	< 1	.055	< 1	.045	< 1	.127
Total acids	28.36**	.649**	4.41*	.320*	11.76**	.480**	37.23**	.699**

* Significant at 5% level.

** Significant at 1% level.

0.604). This indicates that 60.4% of the variability of blackening is due to the ratio of iron to citric acid. Again, this is on the low side for prediction purposes. It is readily apparent that even in blackening potatoes there is always a large excess of citric acid over iron. What, therefore, prevents the citric acid from chelating the iron in blackening potatoes? Hughes and Swain (1962b) discussed this situation and suggested that a mixed complex of iron, chlorogenic acid, and citric acid is perhaps formed. They also recognized the fact that perhaps not all the citric acid in the tuber is free for complex formation, that some may be bound by calcium or other substance.

A possible solution to the problem is suggested by studying the ratio of potassium/citric acid on an equivalent basis. This ratio (stem-end values) is plotted against black-

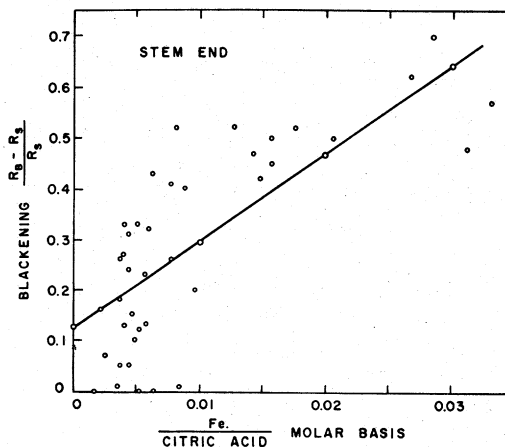


Fig. 3. Variation of degree of discoloration with the ratio of iron content to citric acid content, stem-end values.

ening in Fig. 4, and the *F* values obtained by statistical analysis are presented in Table

Table 4. Summary of statistical study of subgroups (citric acid data).

Subgroups	No. of samples	Stem		Bud		Bud-stem		Bud-stem/ stem	
		F	r	F	r	F	r	F	r
Varieties									
Ontario	8	12.80*	.825*	2.59	.549	< 1	.346	32.33**	.919**
Katahdin	7	7.92*	.782	< 1	.339	3.34	.635	20.33**	.896**
Kennebec	5	2.66	.685	2.08	.640	< 1	0	1.71	.602
State grown									
Wisconsin	19	28.56**	.792**	1.70	.302	6.40*	.524*	36.94**	.828**
Michigan	15	8.19*	.621*	4.25	.490	< 1	.158	19.49**	.774**
Crop year									
1959	14	43.33**	.885**	3.84	.500	5.22*	.549*	37.59**	.874**
1960	19	8.32*	.572*	< 1	.230	1.65	.298	11.34**	.632**
1961	8	6.84*	.730*	2.54	.543	< 1	.303	9.84*	.788*

* Significant, 5% level.

** Significant, 1% level.

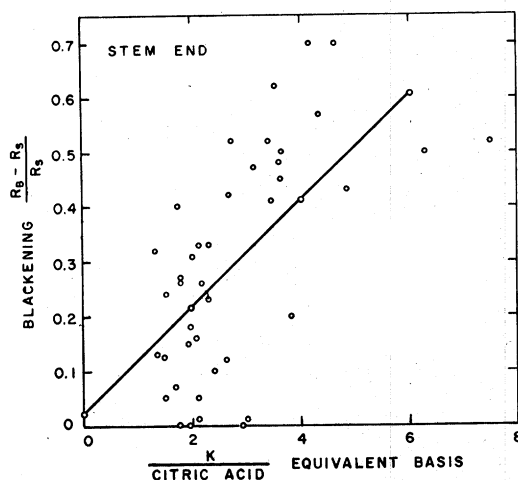


Fig. 4. Variation of degree of discoloration with the ratio of potassium content to citric acid content, stem-end values.

5. The high F values indicate that a highly significant correlation exists between this ratio and degree of discoloration, the larger ratio tending to be associated with the discoloration. Thus, blackening is associated with a large excess of potassium over citric acid. In this role, potassium would act as a blackening inducer. These new data change the role of potassium in the blackening picture from that which was indicated by a previous analytical study (Heisler *et al.*, 1962) in which it was found that the stem end always contained less potassium than the bud end. The study of the ratio of potassium/citric acid on an equivalent basis, however, shows that the citric acid content of the stem end is lower relative to the bud end, than the potassium content. This accounts for the fact that the stem-end ratio is always higher than the bud-end ratio. The role of potassium was further investigated by some *in vitro* experiments. Working with a model system of iron (.030 mmoles) and chlorogenic acid (.045 mmoles) brought to a pH of 6.0 with .050 mmoles

of NaOH (total volume 15 ml), it can be demonstrated that although citric acid (as little as .007 mmoles) completely decolorized the dark blue-green iron-chlorogenic acid solution, an equal amount of potassium citrate did not, and a large excess darkened the solution further. The pH changed from 6.0 to 4.9 on addition of citric acid, and to 6.3 on addition of potassium citrate. Generally the same result was obtained in a system containing 10 ml of 1% aqueous potato extract plus all other reagents mentioned above except NaOH (total volume again = 15 ml). In this case, however, .020 mmole of citric acid was required to effect decolorization, probably because of the buffer effect of the extract. Here the pH was reduced from 4.9 to 4.5 by the citric acid, and raised to 5.2 by the potassium citrate. It appears that potassium may act in two ways. From the fact that potassium citrate does not decolorize the iron-chlorogenic acid solution it follows that if the concentration of potassium and other conditions are such that the citric acid-salt equilibrium is shifted to the salt side, then potassium would act as a blackening inducer by lessening the effect of citric acid. Potassium citrate may also act to enhance the formation of the iron-chlorogenic acid complex by raising the pH. The above work also indicates that the citric acid effect is at least partly due to its lowering of the pH. It should be emphasized, however, that an iron-chlorogenic acid solution is normally blue-green at a pH above 4.0, and that citric acid decolorized the solution at a pH higher than 4.0. Also, the pH of the potato is fairly constant, varying only slightly from sample to sample, normally from pH 5.9 to 6.1.

Even though potassium appears to be an important factor in the blackening mechanism, it is not likely a controlling factor, since there is probably an excess of potas-

Table 5. Summary of statistical study of interrelationships of constituents.

	Stem		Bud		Stem-bud	
	F	r	F	r	F	r
Fe/citric acid molar basis	59.01**	.777**	9.71**	.446**	61.25**	.782**
K/citric acid equiv. basis	25.02**	.625**	7.18*	.394*	24.40**	.621**

* Significant, 5% level.

** Significant, 1% level.

sium available to the potato tuber. The prime consideration as to whether a potato blackens or not is probably the amount of free organic acid (citric, oxalic, phosphoric, malic) present, or potentially present, and this in turn is dependent on the equilibrium constants of the possible reactions involved.

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